PATENT SPECIFICATION

1,128,963

NO DRAWINGS

1,128,963

Date of Application and filing Complete Specification: 17 Aug., 1967.

No. 38016/67.

Application made in United States of America (No. 574,259) on 22 Aug., 1966.

Complete Specification Published: 2 Oct., 1968.

Index at acceptance:—C2 C(2B22, 2D27, 3A7V2A1, 3A7V2F2, 3A7V2L, 3A13A3A4, 3A13A3B1, 3A13A3L, 3A13C3A, 3A13C6A, 3A13C7, 3A13C10C, 3A13C10H, 3C5A1, 3C5C4, 3C5E2)

Int. Cl.:—C 07 c 43/32, C 07 c 149/36

COMPLETE SPECIFICATION

Novel Orthoesters

We, W. R. GRACE & Co., a Corporation organized and existing under the laws of the State of Connecticut, United States of America, of 7, Hanover Square, New York 5, New York, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to novel compounds which possess orthoester groupings, and to methods for their preparation.

Orthoesters of the general formula

$$R—C(OR')_3$$

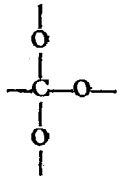
wherein R and R′ represent alkyl or phenyl, have been described in the literature. These compounds readily undergo hydrolysis and hence possess utility as scavengers for acid or water. This property makes orthoesters useful as stabilizers for various compositions wherein it is desired to effectively remove acids and water as they are formed.

Most of the hitherto known orthoester compounds possess relatively low molecular weights and correspondingly high vapour pressures and hence find little application for stabilizers and systems wherein relatively high temperatures are encountered. Furthermore, attempts to increase the molecular weight of orthoesters by mere substitution of larger organic radicals have not been entirely successful. This is due to the fact that the relative stabilizing efficiency of the compound is decreased by increasing molecular weight without increasing the orthoester content.

It is therefore an object of the present invention to provide orthoesters which possess high molecular weight and low vapour pressure, and which have a high orthoester content per given weight of compound.

The orthoesters of the invention find utility as thermal stabilizers for polyvinylchloride resins.

The novel orthoesters of the invention possess at least one of the following grouping:



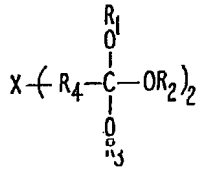
wherein the unsatisfied valencies are filled by organic substituents. These compounds have relatively high molecular weights and contain a high orthoester content per given weight of compound.

[illegible]

Price 75p

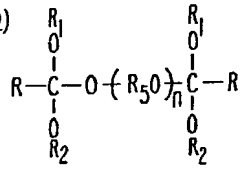
The present invention comprises novel orthoesters having the following general formulae:

(1)



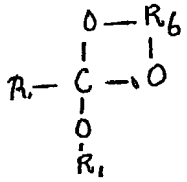
wherein R_1, R_2 and R_3 may be alkyl, phenyl, phenyl-alkyl, alkylphenyl, and alkylphenylalkyl; R_4 may be alkylene phenylene, and alkylphenylene; and X represents oxygen and sulphur.

(2)



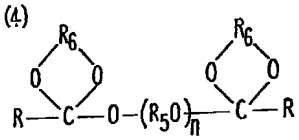
wherein R may represent hydrogen, alkyl, phenyl, phenylalkyl, alkylphenyl-alkyl, halophenyl, nitrophenyl, and alkenyl, and R_1 and R_2 have the meaning given above (1); R_5 may be alkylene, phenylene, alkylalkylene, alkenylene, alkenyl-alkoxyalkylalkylene and alkynylene; and n has a value of from 1 to 4.

(3)



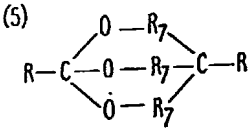
wherein R and R_1 have the meaning given in (1) above; and R_6 may be alkylene, alkylalkylene, and alkenylalkoxyalkylalkylene.

(4)



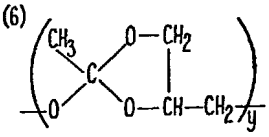
wherein R, R_5, R_6 and n have the meanings given above.

(5)



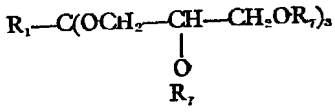
wherein R has the meaning given above and R_7 is alkylene.

(6)



wherein y has a value of from 2 to 10.

(7)



wherein R_7 represents hydrogen or additional orthoester groupings formed during the condensation of from about 0.3 to 3.04 moles of glycerol per mole of tri(loweralkyl)-orthoacetate at a temperature of from about 50 to 200° C. for 0.1 to 72 hours.

The present orthoesters may be conveniently prepared by one of two methods which may be briefly described as (a) an imino ester route and (b) an exchange reaction. These methods are described in detail below.

Iminoester Route

A general synthesis which utilizes iminoesters in the formation of orthoesters is generally set forth in Pinner, Ber. *16* 366, 1644 (1883). In this procedure the appropriate nitriles are reacted in one equivalent of dry hydrogen chloride and one equivalent of alcohol to form an iminoester hydrochloride which is then alcoholized in the excess of alcohol to form the corresponding orthoester. This reaction may be outlined as follows:

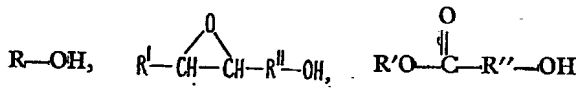
$$RCN + R'OH + HCl \rightarrow R\overset{\overset{N\,H_2Cl}{\|}}{C}OR' + 2R'OH \rightarrow RC(OR')_3 + NH_4Cl.$$

In the above reaction the nitrile substituent R_1 and the alcohol substituent R′ are selected so as to provide the substitution required to form compounds set forth in structures 1 to 7 given above. Typical nitriles used in the above reaction possess the general formula

R CN

wherein R may represent hydrogen, alkyl, phenyl, phenylalkyl, alkylphenyl and alkylphenylalkyl containing up to about 20 carbon atoms. Specific examples of nitriles are hydrogen-cyanide, acetonitrile, propionitrile, lauronitrile, benzonitrile, acrylonitrile.

Typical alcohols used in the above reaction possess the formula

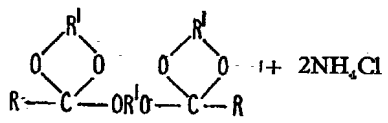


wherein R represents alkyl, phenyl, phenylalkyl, glycidyl alkylphenyl and alkylphenylalkyl containing up to about 20 carbon atoms; R′ represents lower alkyl having up to 4 carbon atoms; and R″ represents alkylene having up to 4 carbon atoms. Specific alcohols used in the above synthesis are methanol, ethanol, propanol, isopropanol, butanol, isobutanol, t-butanol, benzyl alcohol, glycidol, and esters of glycolic acid.

While the above equation represents a synthesis utilizing a monohydric alcohol and a monofunctional nitrile, polyols and polynitriles may be used in either of both steps of the above described synthesis. Such reaction may be indicated as follows:

$$NC—R—CN + 2\,R'—OH + 2\,HCl \rightarrow R'O\overset{\overset{NH_2Cl}{\|}}{C}—R—\overset{\overset{NH_2Cl}{\|}}{C}OR' + 4R'—OH$$
$$\rightarrow (R'O)_3\,CRC\,(OR')_3 + 2\,NH_4Cl \text{ and}$$

$$2\,RCN + HOR'OH + 2\,HCl \rightarrow R\overset{\overset{NH_2Cl}{\|}}{C}—OR'O—\overset{\overset{NH_2Cl}{\|}}{C}R \rightarrow$$



In the above equations R and R′ are selected so as to yield compounds having

the structures set forth as 1, 2, 3, 4, 5, 6, and 7 above. Typical polynitriles and polyols possess the formula

$$NCRCN,\ HOR'OH,\ NCR—X—R—CN,\ HO-(-RO-)_n-H,\ H(CH)_n(OH)—OH$$

wherein R and R' represent alkylene having 1 to 20 carbon atoms, phenylene, and lower alkyl phenylene; X represents oxygen and sulphur; and n has a value of from 1 to 100. Specific examples of polynitriles and polyols which may be employed in the above synthesis are adiponitrile; 2,4-dicyanobutene-1; thiodipropionitrile; oxydipropionitrile; ethylene glycol, propylene glycol; di, tri, and polyethylene glycol; di, tri, and polypropylene glycol; glycerol; neopentyl glycol; 1,4,-butanediol; trimethylolpropane mono alkyl ether; 2-butyne-1,4-diol; and pentaerythritol.

In the above reactions, essentially equivalent amounts of nitrile, alcohol and hydrogen chloride are reacted at a temperature of from $-20°$ to $+75°$ C. The reaction is preferably carried out in the presence of an inert solvent such as chloroform, dichloromethane, ethyl ether, toluene. Generally speaking at the reaction temperatures given above from about 0.1 to about 72 hours are required to achieve the desired iminoester hydrochloride. The resultant iminoester hydrochloride may be recovered by evaporation or filtration of the solvent and washing with a solvent such as ethyl ether.

Upon recovery of the iminoester hydrochloride, it is reacted with an additional two moles of the desired alcohol. This reaction is preferably conducted at a temperature of from 0 to 100° C. in the presence of a solvent such as chloroform, dichloromethane, ethyl ether, or toluene the above temperature conversion of the iminoester hydrochloride to the desired orthoester is completed in from about 1.0 to about 72 hours. The resultant orthoester may be recovered by filtration and subsequent washing with aqueous base with the aid of solvents such as chloroform, dichloromethane, ethyl ether or toluene. The resultant orthoester may be further purified by distillation or crystallization.

Exchange Reaction

A general method for preparing orthoesters which utilizes an exchange reaction is described by Mkhitaryan, J. Gen. Chem. (USSR) *8* 1361 (1938). In this exchange synthesis the alkoxy groups of a readily available orthoester such as triethyl or trimethyl orthoacetate are displaced by higher boiling alcohols or polyols to form the desired orthoester. This reaction may be generally described by the following equation:

$$RC(OR')_3 + 3R''OH \rightarrow RC(OR'')_3 + R'OH$$

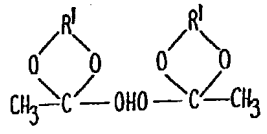
In the above equation the initial orthoester substituents R and R' represent lower alkyl groups having 1 to 4 carbon atoms, preferably methyl or ethyl. The alcohols indicated as R''OH above possess a higher boiling point than the alcohol used in the formation of the orthoester. In the above equation wherein the alcohol is indicated as R''OH, R'' may typically represent alkyl having 1 to 20 carbon atoms, phenyl, alkylphenyl, and phenylalkyl.

Specific examples of alcohols R''OH used in the above equation are propanol, isopropanol, butanol, isobutanol, t-butanol benzyl alcohol, glycidol, and esters of glycolic acid.

The above reaction may also be carried out in two steps using different alcohols or polyols. A typical synthesis of this type wherein the lower alkyl orthoester is first reacted with a polyhydric alcohol indicated as HOROH and secondly reacted with different polyhydric alcohol indicated as HOR'OH may be illustrated as follows wherein methyl triethyl orthoacetate is used as the representative exchangeable orthoester:

$$2\ CH_3C(OC_2H_5)_3 + HOROH \rightarrow CH_3C(OC_2H_5)_2ORO(C_2H_5O)_2CCH_3$$

$$+ 2C_2H_5OH \xrightarrow{+\ 2HOR'OH}$$



$$+ 4C_2H_5OH$$

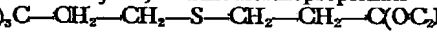
Typical diols which may be used in the above reaction possess the formula HOROH and HOR'OH, wherein R and R' may be different and may typically represent alkylene, phenylene, alkylalkylene, alkenylene, alkyl-alkyloxy-alkalkylene, and alkynylene.

Specific polyols which have been found to be particularly effective in preparing the present novel orthoesters are ethylene glycol, propylene glycol, di-, tri-, and polyethylene glycol, di-, tri-, and polypropylene glycol, glycerol, neopentylglycol, 1,4-butanediol, 1,3-butanediol, trimethylolpropane monoallylether, 2-butyl - 1,4-diol and pentaerythritol. This reaction procedure is particularly effective in preparing the compounds generally set forth as 2, 3, 4, and 6 above.

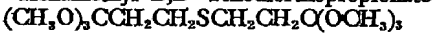
The general conditions used in the above exchange reactions involve reacting substantial equivalents of alcohol and orthoester required to form the desired product. In general, a solution of the desired monohydric and polyhydric alcohol and the lower alkyl orthoester is heated at a temperature of from 20 to 200° C., preferably 50 to 200° C. Generally speaking, using the above reaction temperatures from about 0.1 to about 72 hours are required to obtain the desired exchange orthoester product. Completion of the reaction is readily indicated by collecting the volatile alcohol as it is evolved from the reaction mixture and continuing the heating until the required amount has been collected. The resultant product may be subsequently purified by recrystallization from solvents such as ethyl ether, chloroform, and toluene or by distillation.

Specific examples are hereinafter given to illustrate the preparation of the following novel esters:

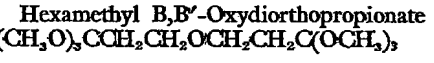
I Hexaethyl B,B'-Thiodiorthopropionate



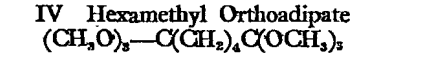
II Hexamethyl B,B'-Thiodiorthopropionate



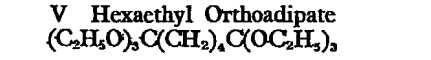
III Hexamethyl B,B'-Oxydiorthopropionate



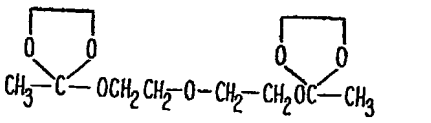
IV Hexamethyl Orthoadipate



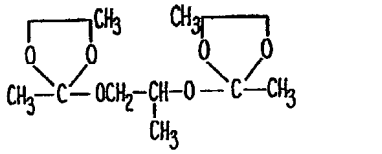
V Hexaethyl Orthoadipate



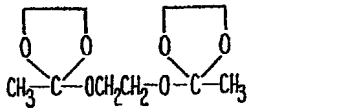
VI 2,2'-(Oxydiethoxy)bis(2-methyl-1,3-dioxolane)



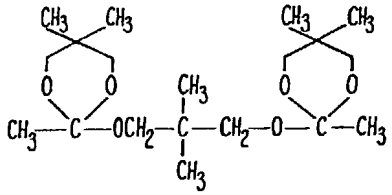
VII Propane 1,2-bis(2-methyl-2-oxy-1,3-dioxolane)



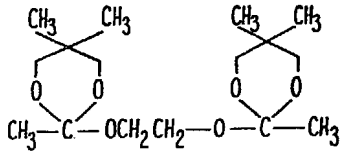
VIII Ethane, 1,2-bis(2-methyl-2-oxy-1,3-dioxolane)



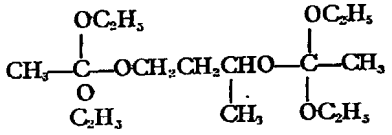
IX 2,2′-(2,2-Dimethyltrimethylenedioxy)bis(2,5,5-trimethyl-m-dioxane



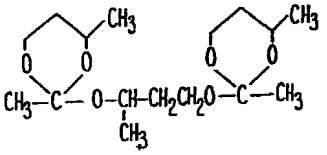
X 2,2′-Ethylenedioxybis(2,5,5-trimethyl-m-dioxane)



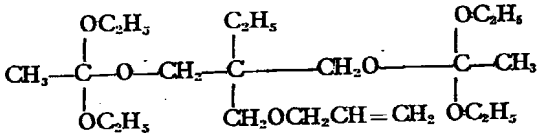
XI 2,2,8,8-Tetraethoxy-4-methyl-3,7-dioxononane



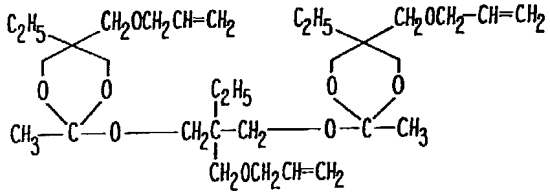
XII 2,2′-(1-Methyl-trimethylenedioxy)bis(2,6-dimethyl-m-dioxane



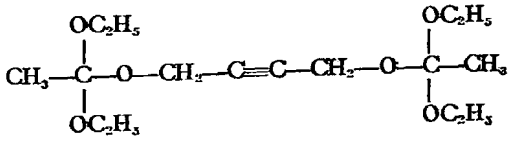
XIII 2,2,8,8-Tetraethoxy-5-ethyl-5-allyloxymethyl-3,7-dioxononane



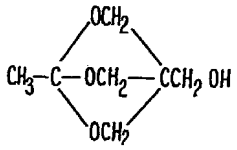
XIV 2,2′-(2-Ethyl-2-allyloxymethyl trimethylenedioxy)bis-(2-methyl-5-ethyl-5-allyloxymethyl-m-dioxane)



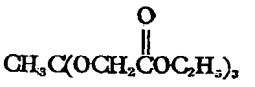
XV 2,2,9,9-Tetraethoxy-3,8-dioxa-5-decyne



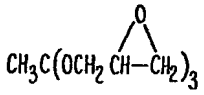
XVI 4-Hydroxymethyl-1-methyl-2,6,7-trioxabicyclo[2,2,2] octane



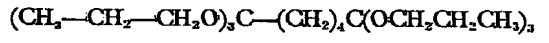
XVII Tris(ethyl glycolate)orthoacetate



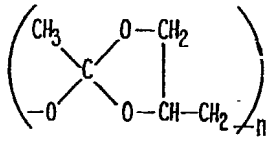
XVIII Tris(glycidol)orthoacetate



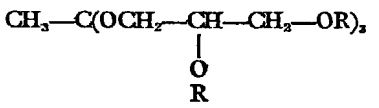
XIX Hexa-n-propyl orthoadipate



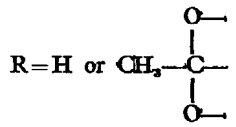
XX Poly(glyceryl orthoacetate)



or



where n = 2 to 10



Most of this product XX has the composition shown by the left-hand formula, but a small part of the product may conform to the right-hand formula.

In the following Examples, references to millimetres (mm.) are to mm. of mercury pressure.

EXAMPLE 1

Preparation of Hexaethyl B,B′-Thiodiorthopropionate

Over a period of 2 hours, 39 g. (1.07 moles) of dry hydrogen chloride was added to a well-stirred solution of 70 g. (0.5 mole) B,B′-thiodipropionitrile, 46 g. (1.0 mole) absolute ethanol and 211 ml of chloroform at 0° to 5° C. There was some liberation of heat, and cooling was required to keep the reaction temperature at 25° C. for several hours. The reaction mixture began to solidify after 3 hours and it was kept at 4° C. overnight. The resultant solidified mass was pulverized and washed twice with 250 ml portions of dry ethyl ether. The product was dried overnight at 25° C. and 60 mm. to give 147 g. (96.5% yield) of a white crystalline solid, melting with decomposition

at 94° to 100° C. The product was assumed to be nearly pure diethyl B,B'-thiodiiminopropionate dihydrochloride.

A solution of 61 g. (0.20 mole) of diethyl B,B'-thiodiiminopropionate dihydrochloride in 400 ml of dry ethanol was stirred for 24 hours at 25° to 30° C. The resultant slurry was filtered free of solids and the solids washed twice with 50 to 100 ml portions of ethyl ether. Drying the solids overnight at 30° to 40° and 60 mm gave 16.4 g. (76.5% yield) of ammonium chloride. The combined filtrate and ether washings were made basic with 7 g. of sodium ethylate. The solids were again filtered from the product slurry and washed with ether. The combined filtrate and ether wasings were washed twice with 100 ml portions of water and then the organic phase was dried over anhydrous magnesium sulphate. The volatile solvents were evaporated from the organic phase and the residual oil was distilled through a 1 inch diameter by 3 inch long column to give as a main fraction 58.1 g. of a pale yellow liquid boiling at 125° to 140° at 0.7 mm.

An orthoester assay of this material gave an average value of 88.8% (calculated as the orthoadipate). The yield of orthoester starting from the diiminoester was 67.5%.

EXAMPLE 2

Preparation of Hexamethyl B,B'-Thiodiorthopropionate

A solution of 70 g. (0.5 mole) B,B'-thiodipropionitrile, 32 g. (1.0 mole) methanol and 200 ml dry dioxane was reacted with 52 g. (1.45 moles) of hydrogen chloride overnight at 0° to 10° C. The resultant solids were pulverized and washed three times with 100 ml portions of dry diethyl ether. The solid product was dried to constant weight overnight at 30° C. and 60 mm to give 132.4 g. (96% yield) of the white crystalline dimethyl B,B'-thiodiiminopropionate dihydrochloride which melts with decomposition at 130° C. to 160° C. The chlorine content of the dihydrochloride (Fajan's method) was 25.6% (theory, 25.4%).

A solution of 845 g. (3.07 moles) of dimethyl B,B'-thiodiiminopropionate dihydrochloride in three liters of absolute methanol was stirred for 16 hours at 45° C. The resultant product slurry was filtered free of ammonium chloride and the ammonium chloride was washed with 500 ml of ethyl ether. Upon drying overnight at 30° C. and 60 mm, 231 g. (4.3 moles, 71% yield) of ammonium chloride were obtained. The combined filtrate and ether washings were made basic with 80 g. (1.5 moles) of sodium methoxide dissolved in methanol. The volatile solvents were removed from the reaction slurry by evaporation at 40° to 45° C. and 20 to 30 mm. The residue was filtered free of solids and the solids were washed with 200 ml of ethyl ether. The combined ether washings and the filtrate were washed twice with 250 ml of water. The organic phase was dried over anhydrous magnesium sulphate and the volatile solvents removed by evaporation at 45° to 50° C. at 60 mm to give 453 g. of pale yellow oil. The product oil was quickly distilled through a column 3 inch long by 1 inch in diameter to give the following fractions:

1. 348 g. colourless oil, boiling 117° to 135° C. at 0.7 mm
2. 10 g. yellow oil, boiling 135° to 150° C. at 0.7 mm
3. 70 g. orange oil which partially solidified after several days

Analyses of the first fraction gave:

Wt. % orthoester (calc. as hexamethyl B,B'-thiodiorthopropionate)), 51.2

Wt. % normal ester (calc. as dimethyl B,B'-thiodipropionate), 57.8

Wt. % nitrile (calc. as adiponitrile), 1.7

Thus, according to the orthoester assay, fraction one represents a 18.3% yield from the iminoester.

EXAMPLE 3

Preparation of Hexamethyl B,B'-Oxydiorthopropionate

The reaction of 62 g. (0.50 mole) B,B'-oxydipropionnitrile, 32 g. (1.0 mole) dry methanol and 37 g. (1.0 mole) dry hydrogen chloride all in 200 ml of chloroform, was conducted just as described for the thio analog in Example 2. 118.5 g. (90.5% yield) of white crystals were obtained, melting with decomposition at 85° to 98° C. This material was assumed to be the desired dimethyl B,B'-oxydiiminopropionate dihydrochloride.

The reaction of 52 g. (0.2 mole) of dimethyl B,B'-oxydiiminopropionate dihydrochloride in 225 ml of dry methanol was conducted as described for the thio analog. After the first 2 hours 10.5 g. (49.4% yield) of ammonium chloride was collected and after 24 hours 5 g. (23.5% yield) more ammonium chloride was collected. After the

usual purification and separation 47.5 g. were obtained of a crude, colourless liquid which upon distillation gave the following fractions:

1. 38.6 g., boiling at 115° to 125° C at 2 mm
2. 2.2 g., boiling at 130° to 175° C at 2 mm
3. 2.0 g. orange, viscous pot residue

Analyses of the first distillation fraction gave the following average values:

Wt. % orthoester (calc. as hexamethyl B,B'-oxydiorthopropionate), 89.1

Wt. % normal ester (calc. as dimethyl B,B'-oxydipropionate), 9.9

Wt. % nitrile (calc. as B,B'-oxydipropionitrile), 1.4

An NMR (nuclear magnetic resonance) analysis of the first fraction showed that the ratio of orthoester peaks heights to those of the normal ester was 10 to 1 (91% orthoester). Thus, according to the orthoester assay the first fraction represents a 61% yield from the diiminoester.

EXAMPLE 4

Preparation of Hexamethyl Orthoadipate

Over a period of 1.5 hours, 410 g. (11.2 moles) of dry hydrogen chloride were passed into a well stirred solution of 540 g. (5.0 moles) adiponitrile and 320 g. (10.0 moles) dry methanol in two litres of chloroform kept at 5° to 20° C. The reactants were stirred at 10° to 20° C. for 20 more hours. The resultant thick slurry was filtered and the solids washed with 400 ml chloroform. Upon drying the solid, 1140 g. (93% yield) of fine white crystals were obtained which melted at 195° to 205° C. with decomposition. The following evidence indicated the product was dimethyl diiminoadipate dihydrochloride.

Analyses

% nitrogen (Kjeldahl method) 11.5 (theory, 11.43)

% chlorine (Schoniger method) 28.6 (theory, 28.93)

Hydrolysis of the diiminoadipate at 25° C. for 16 hours in water buffered to pH 7.0 gave 72.5% yield of dimethyl adipate.

A slurry of 2450 g. (10 moles) of dimethyl diiminoadipate dihydrochloride in 3170 g. (99.0 moles) of dry methanol was stirred at 25° C. for 17 hours. The slurry was thick at first but later changed to a pale yellow solution containing crystals of ammonium chloride (identified by x-ray crystallography). The ammonium chloride was collected by filtration and washed with 300 ml of chloroform to give, when dried, 859 g. (80.5% yield).

The combined filtrate and chloroform washings were washed with three litres of 15% aqueous sodium carbonate. The pH of the aqueous phase was about 8. The aqueous phase was washed three times with one litre portions of chloroform. The combined organic phase and chloroform washings were washed with 1500 ml of water. The organic phase was dried over 200 g. of anhydrous magnesium sulphate and the solids removed by filtration. The volatile components of the filtrate were removed by evaporation at 25° to 40° C and 20 to 30 mm to leave 2078 g. of a pale yellow oil. This crude hexamethyl orthoadipate (minus 10 ml for analyses) was distilled through a 20 inch × 1/2 inch diameter spinning band column to give these fractions:

1. 98 g. boiling at 40° to 135° C. and 13 to 15 mm
2. 273 g. boiling at 135° to 120° C. and 20 to 5 mm
3. 944 g. boiling at 114° to 117° C. and 4.1 to 2.6
4. 344 g. boiling at 117° to 122° C. and 2.4 mm
5. 62 g. boiling at 130° C. and 3.8 mm
6. 6 g. boiling at 127° C. and 7.1 mm
7. 156 g. pot residue, a yellow oil

Analyses of the various fractions gave the following results:

#	Wt. % Ortho Ester (calc. as Orthoadipate)	% Ortho Ester Based on Sites Available	Wt. % Normal Ester (calc. as dimethyl adipate)	Wt. % Nitrile (calc. as adiponitrile)
1	65.6	2.4	28.4	7.2
2	72.9	7.5	22.1	5.4
3	84.4	30.0	13.3	4.0
4	93.6	11.8	1.7	0.7
5	92.5	2.2	1.2	0.5
6	89.2	0.2	3.4	1.2
7	90.3	5.3 / 59.4	7.9	0.7
8	72.0	56.2	10.0	3.4

Fractions 3 and 4 (combined yield of 41.8%) were taken as hexamethyl orthoadipate.

EXAMPLE 5

Preparation of Hexaethyl Orthoadipate

A solution of 540 g. (5.0 mole) daiponitrile, 460 g. (10 moles) absolute ethanol and 750 ml of chloroform was treated with 390 g. (10.7 moles) of dry hydrogen chloride at 0° to 10° C. for 2 hours. The reaction was stirred for 16 hours at 0° to 20° C. The resultant cake was pulverized and the solids collected by filtration. The solids were washed with 500 ml of chloroform and dried for 2.5 days at 25° C. and 60 mm to give 1340 g. (98.0% yield) of the diethyl diiminoadipate dihydrochloride which melted with decomposition at 118° to 125° C.

A slurry of 274 g. (1.0 mole) diethyl diiminoadipate dihydrochloride in 690 g. (15 moles) of dry ethanol was stirred at 25° C. for 20 hours. The solids were filtered off to give 74 g. (69.4% yield) of ammonium chloride. The filtrate in 500 ml of chloroform was washed with 300 ml of 15% aqueous sodium carbonate followed by 250 ml of water. The organic phase was dried over 25 g. of anhydrous magnesium sulphate and the solid removed by filtration. The volatile components of the organic phase were removed by evaporation at 25 to 30° C and 30 to 20 mm. The residual oil was distilled through a 8 inch × 3/4 inch diameter column to give fractions:

1. 42.4 g. boiling at 100° to 110° C. and 2.0 mm
2. 47.2 g. boiling at 115° C. and 2.0 mm
3. 94.9 g. pot residue, a yellow oil

Orthoester analysis of fraction 2 gave the average value of 98.4% (calculated as hexaethyl orthoadipate).

EXAMPLE 6

Preparation of 2,2'-(Oxydiethoxy)bis(2-methyl-1,3-dioxolane)

(a) *Via the iminoester method* — A solution of 530 g. (5.0 moles) of diethylene glycol, 410 g. (10.0 moles) acetonitrile and 750 ml of chloroform was cooled to 0° C. Over a period of 1.0 to 1.5 hours to 365 to 390 g. (10.0 to 10.7 moles) of dry hydrogen chloride were passed into the well stirred solution and the temperature was kept between 0° to 10° C. by cooling the reactor in an ice bath. For 2 to 3 hours after the addition of hydrogen chloride was completed, cooling was required to keep the reaction between 0° and 10° C. The resultant reaction product precipitated as a thick syrup which was not soluble in chloroform, toluene or ethyl ether.

The syrup partially crystallized after 16 hours at 10° C. Upon mixing the product slurry with 1 litre of dry ethyl ether, a solid cake was formed. This cake was pulverized and washed with 1 litre of dry ethyl ether. Upon drying at 25° C. and

30 mm, 1265 g. of the white crystalline diiminoester dihydrochloride (I) was obtained which melted with decomposition at 75° to 80° C.

Assays of the purity of this diiminoester dihydrochloride by several methods gave the average value of 85%. Thus, the yield of ester I was 82.5%.

A slurry of 650 g. (2.5 moles) of ester I in 310 g. (5.0 moles) of ethylene glycol was mixed for 20 hours in a ball mill at 25° C. The resultant slurry was filtered free of solids and the solids were washed with 100 ml of chloroform to give 237 g. (4.4 moles, 89% of theory) of ammonium chloride. The filtrate plus the chloroform washings were washed with 500 ml. of 10% aqueous sodium carbonate followed by 500 ml of water. The organic phase was dried over 50 g. of anhydrous magnesium sulphate. The chloroform was evaporated from the solution and the residue was distilled to give the following fractions:

1. 17 g. boiling at 25° to 95° C at 1.0 mm
2. 334 g. boiling at 95° to 130° at 0.6 mm
3. 1 g. pot residue

An orthoester assay of fraction 2 gave the values of 91.3 and 92.5%. The yield was 43.6%.

The overall yield starting from acetonitrile was 36%.

(b) *Via the exchange method* — A solution of 54 g. (0.5 moles) of diethylene glycol and 162 g. (1.0 moles) of triethyl orthoacetate was heated at 110° C. for several hours. All volatile materials were collected to give 52 ml of distillate which was shown by gas chromatography to be essentially all ethanol. This represents about 89% of the theoretical amount of ethanol to be evolved in the first step of the exchange reaction. Distillation of the pot residue gave the following fractions:

1. 54.9 g. boiling at 25° to 85° C. at 0.4 mm
2. 60.8 g. boiling at 85° to 125° C. at 0.5 mm
3. 25.2 g. pale yellow pot residue

Fractions 2 and 3 had infrared and NMR spectra very nearly the same as this orthoester prepared by the diiminoester route. The combined fractions, 2 and 3 (865 g.) represented a 64% yield starting from triethyl orthoacetate.

EXAMPLE 7

Preparation of Propane, 1,2-bis(2-methyl-2-oxy-1,3-dioxolane)

A mixture of 81 g. (0.5 moles) triethyl orthoacetate and 57 g. (0.75 moles) 1,2-propanediol in 50 ml benzene containing 0.5 g. p-toluene sulphonic acid was refluxed. The benzene which distilled was analysed for ethanol gas gas chromatography. Fresh benzene was periodically added to the pot. After 4 hours 79.2 g. (90% of theory) of ethanol was collected.

The last traces of benzene and ethanol were removed at 60° C. and 10 to 20 mm to give 76 g. crude product oil. This material was washed with 40% aqueous sodium carbonate and twice with water. The aqueous washings were washed with chloroform and the combined organic phases were dried over anhydrous magnesium sulphate. Evaporation of the chloroform left 74.1 g. crude oil which contained 64.9—65.8% orthoester. Distillation of 60.5 g. of this oil gave:

Fraction	b.p. °C.	pressure, mm	weight, g.
#1	44—50	1.0	14.1
#2	55—68	1.0	5.9
#3	77—87	0.8	9.9
#4	87	0.6	5.7

Fractions 3 and 4 represent a 24% yield of substantially pure orthoester.

The above reaction was repeated without the aid of benzene and p-toluene sulphonic acid. The reactants had to be heated from 110° C. to 140° for 4 hours to remove 94% of the theoretical amount of benzene. A 54% yield of the reasonably pure orthoester (see fractions 3 and 4 above) was obtained.

EXAMPLE 8

Preparation of Ethane, 1,2-bis(2-methyl-2-oxy-1,3-dioxolane)

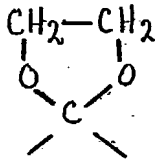
A mixture of 81 g. (0.5 moles) of triethyl orthoacetate and 15.5 g. (0.25 moles) of ethylene glycol was heated at 135° C. for two hours, and 22 g. (96% of theory) of ethanol were released. Thirty-one g. (0.5 mole) of ethylene glycol were added and heating continued for two more hours to release 33 g. (71% of theory) of ethanol.

Distillation of the crude product gave:

Fraction	b.p. °C.	pressure, mm	weight, g.
#1	25—45	0.25	25
#2	50—60	0.25	10
#3	90	0.25	22.8

Fraction 3 solidified to a white crystalline product, m.p. 32—35° C. which asayed 94% orthoester. The infrared spectrum of this material had no carbonyl or hydroxyl absorptions. Its NMR spectrum agreed with the proposed structure.

NMR Analysis

Ratio of Protons				
Theory	Observed	τ Value	Multiplicity	Functional Group
1	1	6.5	singlet	—O—CH_2—CH_2—O—
1.5	1.4	8.5	singlet	—CH_3—
2	1.97	6.0	multiplet	

EXAMPLE 9

Preparation of 2,2'-(2,2-Dimethyltrimethylenedioxy)bis(2,5,5-trimethyl-m-dioxane)

A mixture of 81 g. (0.5 mole) triethyl orthoacetate and 78 g. (0.75 mole) of neopentyl glycol was heated at 140° C. for 3 hours to release 64.8 g. (93.5% of theory) of ethanol.

Distillation of the residue gave:

Fraction	b.p. °C.	pressure, mm	weight, g.
#1	75—110	0.25	25.0
#2	125—130	0.25	35.2
#3	pot		

Fraction 2 (39% yield) solidified into a white crystalline solid, m.p. 78—80° C., which assayed 93% orthoester.

EXAMPLE 10

Preparation of 2,2'-Ethylenedioxybis(2,5,5-trimethyl-m-dioxane)

A solution of 162 g. (1.0 mole) triethyl orthoacetate and 31 g. (0.5 mole) ethylene glycol was heated at 140° C. for several hours to evolve 46 g. (100% of theory) of ethanol. To the pot residue was added 104 g. (1.0 mole) neopentyl glycol, and the heating was continued at 140° C. for several hours until 92 g. (100% of theory) of ethanol was distilled. The crude product (151 g. 94% yield, 84% orthoester) distilled at 90—110° C. at 0.25 mm to give a white crystalline solid melting at 25° C.

EXAMPLE 11

Preparation of 2,2,8,8-Tetraethoxy-4-methyl-3,7-dioxanonane

A solution of 162 g. (1.0 mole) of triethyl orthoacetate and 90 g. (0.5 mole) of 1,3-butanediol was heated at 140° C for several hours until 46 g. (100% of theory) of ethanol distilled off. The residue was distilled at 25—35° C. and 0.5 mm to give 132 g. (83.5% yield, 96.4% orthoester analysis) of the colourless liquid product. The infrared spectrum of this material showed neither hydroxyl nor carbonyl absorption.

EXAMPLE 12

Preparation of 2,2'-(1-Methyl-trimethylenedioxy)bis(2,6-dimethyl-m-dioxane)

A solution of 162 g. (1.0 mole) triethyl orthoacetate and 135 g. (1.5 moles) 1,3-butanediol was heated at 140° C for several hours until ethanol (121 g. 88% of theory) no longer distilled. Distillation of the crude residue gave 67 g. (21% yield, 95.2% orthoester assay) of a colourless oil boiling at 31—40° C. and 0.35 mm.

EXAMPLE 13

Preparation of 2,2,8,8-Tetraethoxy-5-ethyl-5-allyloxymethyl-3,7-dioxononane

A solution of 162 g. (1.0 mole) of triethyl orthoacetate and 87 g. (0.5 mole) of trimethylolpropane monoallyl ether was heated at 140° C. until 46 g. (100% of theory) of ethanol distilled. Distillation of the residue gave 197 g. (50.5% yield, 80.1% orthoester assay) of a colourless oil boiling at 75° to 80° C. and 0.25 mm.

EXAMPLE 14

Preparation of 2,2'-(2-Ethyl-2-allyloxymethyl trimethylenedioxy)bis. (2-methyl-5-ethyl-5-allyloxymethyl-m-dioxane)

A solution of 162 g (1.0 mole) of triethyl orthoacetate and 261 g. (1.5 moles) of trimethylolpropane monoallyl ether was heated at 170° C. until ethanol (130 g. 94% of theory) no longer distilled. The high-boiling residue weighed 244 g. (85% yield) and assayed 79% orthoester.

EXAMPLE 15

Preparation of 2,2,9,9-Tetraethoxy-3,8-dioxa-5-decyne

A mixture of 324 g. (2.0 moles) triethyl orthoacetate and 86 g. (1.0 mole) 2-butyne-1,4-diol was heated at 140° C. for several hours until 92 g. (100% of theory) of ethanol distilled. Distillation of the product residue gave 126 g. (40% yield) of a colourless oil boiling at 112°—130° C. and 0.5 mm which assayed 54% orthoester.

EXAMPLE 16

Preparation of 4-Hydroxymethyl-1-methyl-2,6,7-trioxabicyclo[2,2,2]octane

A mixture of 162 g. (1.0 mole) triethyl orthoacetate and 136 g. (1.0 mole) pentaerythritol was heated for several hours at 160° C. until 45.5 g. (99% of theory) of ethanol distilled. The product residue (145 g., 91% yield) was a white crystalline solid which melted at 80°—85° C. and assayed 83.7% orthoester.

EXAMPLE 17

Preparation of Tris(ethyl glycolate)orthoacetate

A solution of 50 g. (0.31 mole) triethyl orthoacetate and 98 g. (0.93 mole) ethyl glycolate was heated at 120° C for several hours until the ethanol (38.5 g., 90% of theory) no longer distilled. Distillation of the product residue gave 14.5 g. (14% yield) of a colourless oil boiling at 115°—135° C. and 0.5 mm which assayed 92% orthoester.

EXAMPLE 18

Preparation of Tris(glycidol)orthoacetate

A mixture of 81 g. (0.5 mole) triethyl orthoacetate and 111 g. (1.5 moles) glycidol was heated at 130° C. for several hours until ethanol 54.5 g., 81% of theory) no longer

distilled. Distillation of the product residue gave 29.5 g. (24% yield) of a colourless oil boiling at 130° C. and 0.25 mm which assayed 96.5% orthoester.

EXAMPLE 19

Preparation of Hexa-n-propyl orthoadipate

A solution of 119 g. (0.5 mole) of hexamethyl orthoadipate in 500 ml of n-propanol was heated at 120° C. for several hours until gas chromatographic analysis of the propanol distillate showed that it no longer contained methanol. About 90% of the theoretical amount (3 moles) of methanol was collected. Distillation of the residue gave 93 g. (43% yield) of a colourless oil boiling at 120°—142° C. and 1.0 mm which assayed 78% orthoester.

EXAMPLE 20

Preparation of Poly(glyceryl orthoacetate)

The following table lists some reactions of glycerol (95—96%, 3—4% water) with triethyl orthoacetate (TEOA). In all cases 90—100% of the required amount of ethanol was distilled during the reaction. In several reactions the addition of a small amount of a monofunctional alcohol (cetyl alcohol) succeeded in keeping the molecular weight, and therefore the viscosity, of the product at a more manageable level.

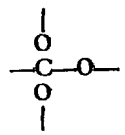
The properties of the products are given in the table, including the ratio of the infrared (IR) spectra at 3400 and 2900 cm^{-1}.

Run	Method of Preparation	% Yield and colour	Orthoester content (% of theory)	IR $\frac{OH(3400CM^{-1})}{CH(2900CM^{-1})}$	Viscosity @ 25° Centipoise (Brookfield)
1	0.5 moles TEOA + 0.75 moles glycerol at 110° to 120°C. for 5—6 hrs. 1 atm.	79.0 colourless	83.5	1.871	9940
2	50 moles glycerol added over 3 hrs. to 50 moles TEOA at 130°C. and 1 atm. Heated 3 more hrs. at 130—180°C. and 1 atm.	92.0 orange	67.0	1.236	28250
3	1.0 mole glycerol added over 3 hours to 1.0 mole TEOA at 130°C. to 140°C. and 1 atm. Last 25% EtOH removed at 10 to 1 mm.	100 colourless	68.5	1.054	12440
4	1.0 mole TEOA and 1.0 mole glycerol + 0.004 moles cetyl alcohol at 130° to 140°C. for 5 to 6 hrs.	96.0 colourless (hazy)	72.0	0.985	12200
5	1.0 mole TEOA added to 1.0 mole glycerol + toluene over 3 to 4 hrs. at 120°C. EtOH distilled over with toluene.	100 colourless	78.2	0.461	45500
6	1.05 moles TEOA added over 2 hrs. to 1.0 mole glycerol at 100° to 110°C. Final 25% EtOH removed at 90° to 100° @ 10 to 1 mm.	100 colourless	83.4	0.686	73000
7	26.2 moles TEOA added over 4 to 5 hrs. to 25.0 moles glycerol at 90° to 100°C. + 1 atm. Final 25% EtOH removed over 3 hrs. at 90°C. to 100°C. and 10 to 1 mm.	93	79.0	0.616	91500
8	26.2 moles TEOA added over 4 to 5 hrs. to 25.0 moles glycerol plus 0.1 mole cetyl alcohol at 90° to 100° C and 1 atm. Final 25% EtOH removed over 3 hrs. at 90° to 100°C. and 10 to 1 mm.	100 colourless	76.5	0.843	18000

The orthoesters prepared according to the present invention are useful as thermal stabilizers for polyvinylchloride (PVC) when the orthoesters are added in amounts varying from about 0.5 to 10% by weight of PVC, they retard the decomposition of PVC resins during high temperature fabrication thereof. Furthermore, due to the fact the components of the present orthoesters are non-toxic it is found these stabilizers make possible an effective PVC stabilizer system which is non-toxic.

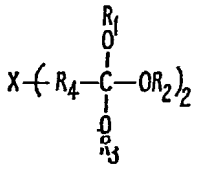
WHAT WE CLAIM IS:—

1. An orthoester having at least one of the groupings



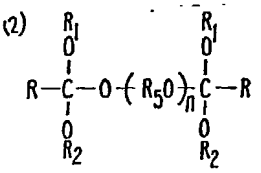
and selected from compounds of the general formulae:

(1)



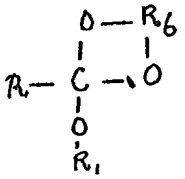
wherein R_1, R_2, and R_3 are each independently alkyl, phenyl, phenylalkyl or alkylphenylalkyl; R_4 is alkylene, phenylene or alkylphenylene; and X is oxygen or sulphur:

(2)



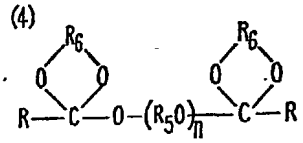
wherein R is hydrogen, alkyl, phenyl, phenylalkyl, alkylphenylalkyl, halophenyl, nitrophenyl or alkenyl; R_1 and R_2 are each independently alkyl, phenyl, phenylalkyl or alkylphenylalkyl; R_5 is alkylene, phenylene, alkylalkylene, alkenylene, alkenylalkoxyalkylalkylene or alkynylene; and n is an integer of 1 to 4:

(3)



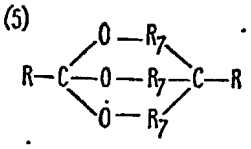
wherein R is hydrogen, alkyl, phenyl, phenylalkyl, alkylphenylalkyl, halophenyl, nitrophenyl or alkenyl; R_1 is alkyl, phenyl, phenylalkyl or alkylphenylalkyl; and R_6 is alkylene, alkylalkylene, and alkenylalkoxyalkylalkylene;

(4)



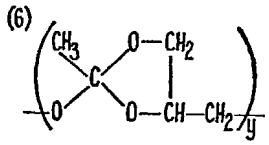
wherein R is hydrogen, alkyl, phenyl, phenylalkyl, alkylphenylalkyl, halophenyl, nitrophenyl or alkenyl; R_5 is alkylene, phenylene, alkylalkylene, alkenylene, alkenylalkoxyalkylalkylene and alkynylene; and R_6 is alkylene, alkylalkylene or alkoxyalkylalkylene; and n is an integer of from 1 to 4;

(5)



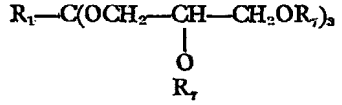
wherein R is hydrogen, alkyl, phenyl, phenylalkyl, alkylphenylalkyl, halophenyl, nitrophenyl or alkenyl; and R_7 is alkylene;

(6)



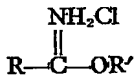
wherein y is 2 to 10;

(7)

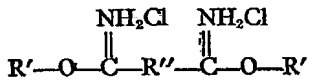


wherein R_7 is hydrogen or is an additional orthoester grouping formed during the condensation of from about 0.3 to 3.0 moles of glycerol per mole of tri(lower alkyl)-orthoacetate at a temperature of from about 50° to 200° C. for a period of in excess of 0.1 hours to 72 hours.

2. Hexaethyl B,B′-Thiodiorthopropionate.
3. Hexamethyl B,B′-Thiodiorthopropionate.
4. Hexamethyl B,B′-Oxydiorthopropionate.
5. Hexamethyl Orthoadipate.
6. Hexamethyl Orthoadipate.
7. 2,2′-(Oxydiethoxy)bis(2-methyl-1,3-dioxolane).
8. Propane, 1,2-bis(2-methyl-2-oxy-1,3-dioxolane).
9. Ethane, 1,2-bis(2-methyl-2-oxy-1,3-dioxolane).
10. 2,2′-(2,2-Dimethyltrimethylenedioxy)bis(2,5,5-trimethyl-m-dioxane).
11. 2,2′-Ethylenedioxybis(2,5,5-trimethyl-m-dioxane).
12. 2,2,8,8-Tetraethoxy-4-methyl-3,7-dioxononane.
13. 2,2′-(1-Methyl-trimethylenedioxy)bis(2,6-dimethyl-m-dioxane).
14. 2,2,8,8-Tetraethoxy-5-ethyl-5-allyloxymethyl-3,7-dioxononane.
15. 2,2′ - (2 - Ethyl - 2 - allyloxymethyltrimethylenedioxy)bis(2 - methyl - 5-ethyl - 5 - allyloxymethyl - m - dioxane).
16. 2,2,9,9 - Tetraethoxy - 3,8 - dioxa - 5 - decyne.
17. 4 - Hydroxymethyl - 1 - methyl - 2,6,7 - trioxabicyclo[2,2,2]octane.
18. Tris(ethyl glycolate orthoacetate).
19. Tris(glycidol)orthoacetate.
20. Hexa-*n*-propyl orthoadipate.
21. Poly(glyceryl) orthoacetate.
22. An orthoester as claimed in claim 1 and substantially as hereinbefore described.
23. A method for preparing an orthoester as claimed in any of the preceding claims which comprises reacting an iminoester hydrochloride of the formula:



or



wherein R and R′ represent alkyl groups which may be the same or different and R″ represents alkylene, with a polyhydric alcohol, and recovering the orthoester formed thereby.

24. A method for preparing an orthoester according to any of claims 1 to 22 which comprises reacting an orthoester of the formula:

$$R—C(OR)_3$$

(wherein R is an alkyl group of 1 to 4 carbon atoms) with a polyhydric alcohol.

25. A method according to claim 24, wherein the alcohol is glycerol.

26. A method according to claim 24 or 25, which is carried out at a temperature of 50 to 200° C.

27. A method for preparing an orthoester, substantially as hereinbefore described with reference to any of the foregoing Examples.

J. A. KEMP & CO.,
Chartered Patent Agents,
14, South Square, Gray's Inn, London, W.C.1.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1968.
Published by the Patent Office, 25 Southampton Buildings, London, W.C.2, from which copies may be obtained.